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ORIGINAL ARTICLE

Combined treatment of retting flax wastewater using Fenton oxidation and granular activated carbon

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Abstract The process of retting flax produces a huge amount of wastewater which is characterized with bad unpleasant smell and high concentration of organic materials. Treatment of such waste had always been difficult because of the presence of refractory organic pollutants such as lignin. In this study, treatment of retting wastewater was carried out using combined system of Fenton oxidation process followed by adsorption on granular activated carbon (GAC). The effects of operating condition on Fenton oxidation process such as hydrogen peroxide and iron concentration were investigated. In addition, kinetic study of the adsorption process was elaborated. The obtained results indicated that degradation of organic matters follows a pseudo-first order reaction with regression coefficient of 0.98. The kinetic model suggested that the rate of reaction was highly affected by the concentration of hydrogen peroxide. Moreover, the results indicated that the treatment module was very efficient in removing the organic and inorganic pollutants. The average percentage removal of chemical oxygen demand (COD), total suspended solid (TSS), oil, and grease was 98.60%, 86.60%, and 94.22% with residual values of 44, 20, and 5 mg/L, respectively. The treated effluent was complying with the National Regulatory Standards for wastewater discharge into surface water or reuse in the retting process.

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1. Introduction

Flax (*Linum usitatissimum* L.) is the main source of high quality bast fibers of which linen is produced. Egypt is considered one of the oldest countries in farming and manufacturing flax. The history goes back to the Ancient Egyptian.

Flax can be used in many industrial sectors like textile, linseed oil, flax seed oil, pulp and paper production and composite materials (Van Dam et al., 1994). However, the conventional growing of flax pollutes water via a process called "retting". Retting is an enzymatic process of rotting away the inner layer of flax from the stalk. The traditional way of water retting is done in manmade water pools, rivers or ponds. During this natural degumming process, butyric acid, methane and hydrogen sulfide are created with a strong rotten smell. If the water is released into nature without treatment, it causes water pollution. Treatment of such wastewater has always been a difficult process because of the refractory organic compounds such as lignin. There are many studies regarding the treatment of flax retting wastewater such as the use of up flow anaerobic sludge blanket (UASB) conducted with membrane bioreactor (MBR) (Liu Shi-qing et al., 2009). Also, Yan (2011) studied the treatment of retting flax wastewater using air flotation/fly/soil-percolation process. It was found that, the maximum removal rate of COD and lignin removal was 95–98% and 80–89% (Zhao and Fan, 2008). They also suggest the application of pretreatment of the flax producing wastewater by hydrolytic acidification process prior to further treatment. Furthermore, electro catalysis-oxidative degradation of pretreated fiber flax wastewater was studied by using three-dimension electrodes which were made of $Ce/RuO_2/SnO_2$-Sb_2O_3/Ti anode.

Recently, the development of novel treatment methods such as advanced oxidation processes (AOPs) has been considered for the oxidation of hardly degraded organic pollutants. Among various AOPs, the Fenton oxidation process (H_2O_2/Fe^{2+}) is one of the most effective decontamination method of organic pollutant. The Fenton oxidation process has been found to be effective for treating various industrial wastewaters (Mantzavinos and Psillakis, 2004). It has the advantage of coagulation and catalytic oxidation, as well as being able to generate oxygen in water. Fenton and photo-Fenton processes have proven to yield very good results either for complete mineralization or destruction of organic compounds (Comninellis et al., 2008). However, there are no previous studies investigating the effects of treating flax wastewater treatment using Fenton oxidation process. Therefore, the aim of this study was to treat a real retting flax wastewater in an attempt to reduce the organic load to a level that complies with the National regulatory standards for wastewater discharge into the surface water or reuse in retting flax process.

2. Materials and methods

2.1. Sources of wastewater

Wastewater produced from a retting flax industry provided material of this study. The company produces 5000 tons/year fibers. The flax retting process was carried out in 32 open ponds and another 32 closed basins. Duration of retting process was ten days in summer and fifteen days in winter. The wastewater from retting flax was discharged into a nearby agricultural drain without any treatment. The wastewater produced was highly contaminated with organic matters as well as suspended solids.

2.2. Collection of samples and analysis

Due to great variation in the quantity and quality of wastewater produced from the retting process, a continuous monitoring program was carried out for almost four months. Composite samples from the end-of-pipe of the flax retting basins were collected and analyzed according to standard method, (APHA, 2005).

2.3. Treatability studies

The retting flax wastewater was treated via Fenton's oxidation followed by adsorption on granular activated carbon (GAC). Equalization was required prior to the oxidation process. Fig. 1 illustrates a schematic diagram of the treatment module. All chemicals used for Fenton oxidation process were of reagent grade purchased from Merck Chemical Company.

2.3.1. Fenton reaction

Fenton reaction essentially depends on three factors: temperature, hydrogen peroxide concentration and Fe^{2+} concentration. Fenton process was carried out at room temperature in order to determine the optimal operating conditions of Fenton reagent (H_2O_2/Fe^{2+}). The pH values of wastewater were adjusted in the range of 3–3.5 with the addition of 1 M H_2SO_4 or 1 M NaOH before chemical oxidation process. $FeSO_4{\cdot}7H_2O$ was added to obtain the desired Fe^{2+} concentration. Finally, H_2O_2 (35% (w/v)) was carefully added to start the Fenton reaction. The aqueous solution of Fenton reagent and wastewater was magnetically stirred during the reaction period. Predetermined amounts of H_2O_2 (35%) and ferrous sulfate ($FeSO_4{\cdot}7H_2O$) were added to wastewater. After Fenton oxidation process, pH of treated wastewater was adjusted to pH 7 by the addition of 10% lime ($Ca(OH)_2$). Lime was added under continuous stirring at a speed of 200 rpm, for duration of 2 min, followed by slow mixing at a speed of 20 rpm, for duration of 20 min, and finally settling for 60 min. The performance of raw wastewater and treated effluent was evaluated in terms of COD removal.

2.3.2. Post treatment using granular activated carbon

The effluent after Fenton treatment was post treated using GAC. Each batch adsorption study was carried out at room temperature (25 ± 0.1 °C). The effects of pH, adsorbent dosage and contact time were studied, using a mechanical shaker at 200 rpm. All samples were filtered through a filter paper (Whatman, No. 42) and the COD was determined in the filtrate. All experiments were carried out in triplicate and the means of the quantitative results were used for further calculations. For the calculation of mean value, the percent relative standard deviation for results was calculated and if the value of standard deviation for any sample was greater than 5%, data were excluded.

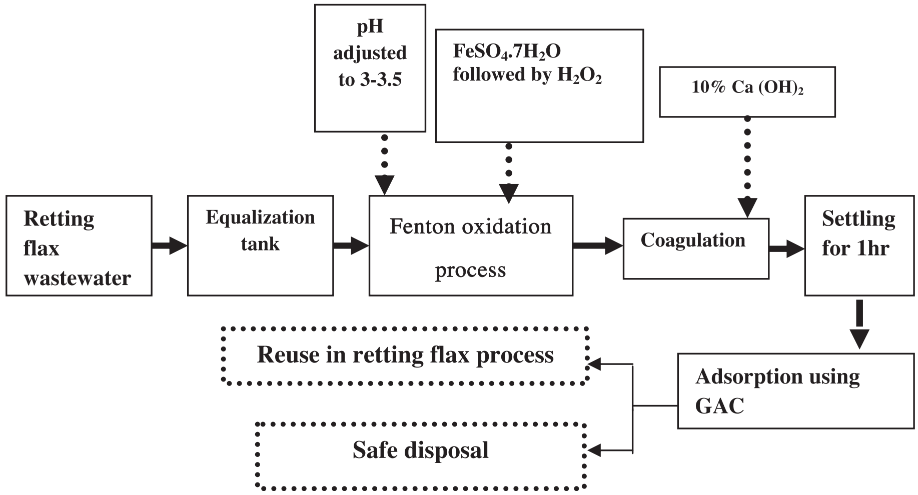

Figure 1 Schematic diagram of treatment module for the retting flax wastewater.

3. Results and discussion

3.1. Characterization of raw wastewater

The physiochemical characteristics of retting flax wastewater are shown in Fig. 2. The results indicated that the concentration of chemical oxygen demand (COD) ranged between 127 and 6718 mgO_2/l with an average value of 3133 mg/L. Moreover, the average biodegradable matters as indicated by BOD were 1464 mg/L. The average BOD/COD ratio was 0.467 which indicated some difficulties in biodegradation. In addition, the total suspended solids reached 149 mg/L.

3.2. Fenton oxidation

The Fenton oxidation reaction involves the application of ferrous ions to react with hydrogen peroxide producing hydroxyl radicals (.OH) with a powerful oxidizing ability to degrade organic pollutants. The mechanism of the Fenton reaction is still under intense and controversial discussion. Generation of .OH by the dark reaction of H_2O_2 with ferrous salt has been the subject of numerous studies during the last decade (Chan and Chu, 2003). The general mechanism using Fenton reagent by which the hydroxyl radicals are produced is a number of cyclic reactions, utilizing the Fe^{2+} or Fe^{3+} ions as a catalyst to decompose the H_2O_2. These ions are regenerated in their original state at the end of the cyclic reactions according to the following equations.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\cdot}OH + OH^{-} \quad (1)$$

$$Fe^{2+} + {}^{\cdot}OH \rightarrow Fe^{3+} + OH^{-} \quad (2)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe - OOH^{2+} + H^{+} \quad (3)$$

$$Fe - OOH^{2+} \rightarrow Fe^{2+} + {}^{\cdot}OOH \quad (4)$$

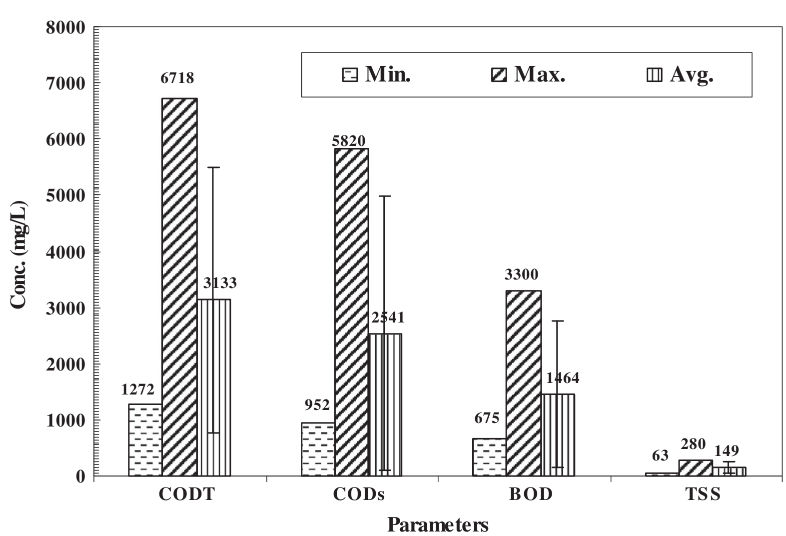

Figure 2 Analysis of raw flax retting wastewater for duration of four months.

$$Fe^{2+} + {}^{\cdot}OOH \rightarrow Fe^{3+} + {}^{-}OOH \quad (5)$$

$$Fe^{3+} + {}^{-}OOH \rightarrow Fe^{2+} + O_2 + H^+ \quad (6)$$

$$H_2O_2 + {}^{\cdot}OH \rightarrow Fe^{2+} + {}^{\cdot}OOH \quad (7)$$

3.2.1. Effects of H_2O_2:COD ratios on the wastewater degradation by Fenton process

Used chemicals are major operational cost items for many wastewater treatment facilities (Gulsen and Turan, 2004; Zhang et al., 2005). Therefore, it is necessary to assess readily in terms of both the absolute concentration of reagents (i.e. hydrogen peroxide and ferrous ions) and the molar ratio (H_2O_2/Fe^{2+}). It should be noted that the removal of organic materials from wastewater is enhanced as the dose of used chemical increases. However, the amount of increase becomes negligible when the dosage is increased above a certain required level (Deng and Englehardt, 2006; Zhang et al., 2005).

Excessive application of hydrogen peroxide generates gas bubbles, which inhibits sludge sedimentation (Deng and Englehardt, 2006; Lau et al., 2001). Moreover, bacteria will be disintegrated in case of the presence of excess hydrogen peroxide and that may inhibit biological treatments (Gogate and Pandit, 2004). Thus, it is necessary to optimize the hydrogen peroxide dosage via investigation of effect of H_2O_2:COD ratio on Fenton oxidation of flax wastewater. Several experiments were carried out by varying the H_2O_2 amount at a constant concentration of COD and constant Fe^{2+}:H_2O_2 (1:50) ratio. The investigated ratio was 0.55, 0.75, 1.1, and 2.2.

Fig. 3 illustrates the percentage of COD removal as a function of time at different H_2O_2:COD ratios. The obtained results showed that the percentage of COD degradation increases with increase in the ratio of H_2O_2:COD up to 0.75. This may be attributed to the increase in H_2O_2 dose, which increases the amount of generated •OH. Moreover, increasing the H_2O_2/COD ratio to more than 0.75 M leads to a considerable decrease in COD removals. Decrease in COD removal was achieved because H_2O_2 acts as a hydroxyl radical scavenging nature of hydrogen peroxide towards •OH (Eqs. 8 and 9) (Niaounakis and Halvadakis, 2006). Therefore, it will decrease the •OH concentration in the system.

$$H_2O_2 + {}^{\cdot}OH \rightarrow {}^{\cdot}HO_2 + H_2O \quad (8)$$

$${}^{\cdot}HO_2 + {}^{\cdot}OH \rightarrow H_2O + O_2 \quad (9)$$

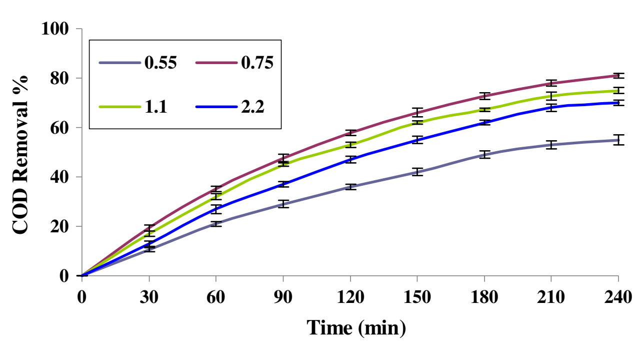

Figure 3 Effects of H_2O_2:COD on Fenton oxidation process of wastewater, reaction time 120 min; pH 3, Fe(II):H_2O_2 1:50.

In addition, this may be due to auto-decomposition of H_2O_2 to oxygen and water and the recombination of OH radicals as follows:

$$2H_2O_2 \rightarrow 2H_2O + O_2 \quad (10)$$

$${}^{\cdot}OH + H_2O \rightarrow H_2O + HO \quad (11)$$

Therefore, optimal concentration of H_2O_2 should be added to achieve the best degradation. From the economical point of view, the optimum H_2O_2:COD ratio for the oxidation of wastewater was selected to be 0.75 as shown Fig. 3.

3.2.2. Effects of H_2O_2:Fe^{2+} ratios on the wastewater degradation by Fenton process

Degradation efficiency using Fenton process for retting flax wastewater is also influenced by the concentration of Fe^{2+} ion which catalyzes hydrogen peroxide decomposition resulting in •OH radical production and consequently the degradation of organic materials. Generally, an extreme dosage of iron can contribute to a significant increase in sludge. Excessive iron salt dosing requires further treatment of the effluent before its discharge into receiving water (Gogate and Pandit, 2004). Fig. 4 shows the effect of reagents concentration of H_2O_2/Fe^{2+} ratio on COD removal. A low H_2O_2/Fe^{2+} ratio provided high efficiency of Fenton treatment of flax wastewater. Removal of COD increased rapidly from 74% to 85% with increasing iron concentration (H_2O_2/Fe^{2+} ratio, 100 to 25). However, a slight increase in COD concentration (3%) was achieved upon further decrease in H_2O_2/Fe^{2+} ratio above 10 (COD removal was ≈88% with insignificant difference from H_2O_2/Fe^{2+} ratio = 25). Removal rate of COD at a high ferrous iron concentration was quicker than that at the lower level. At the beginning of the Fenton process, all ferrous ions reacted quickly with hydrogen peroxide according to Eq. (1), with a rate constant that was much higher than that of the reaction shown in Eq. (2). As a result, there was a rapid generation of hydroxyl radicals, which in turn led to rapid oxidation of the organic compounds and quick depletion of ferrous ions. The availability of ferrous ions becomes the main rate-limiting step in the process as that is the reduction of ferrous into ferric ion. In fact, further increase of the Fe^{2+}:H_2O_2 ratio

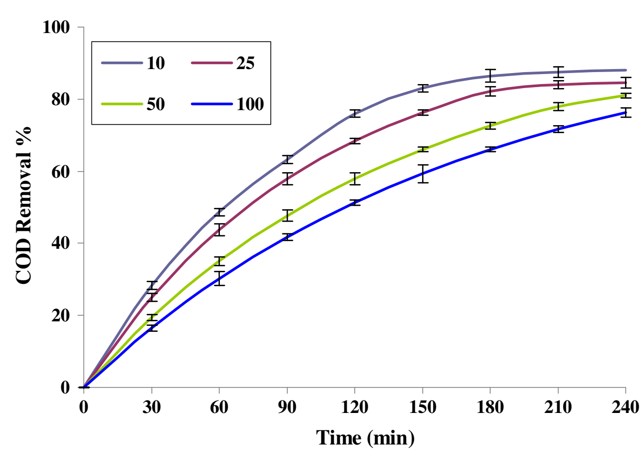

Figure 4 Effects of H_2O_2:Fe^{2+} on Fenton oxidation process of wastewater, reaction time = 120 min; pH = 3, COD:H_2O_2 = 1:0.75.

actually decreases the extent of the degradation of wastewater. Thus, the optimal ratios of Fe^{2+}:H_2O_2 is 10 for the treatment of flax wastewater by the Fenton treatment. In this case, Fe^{2+} reacted with •OH radicals as a scavenger according to Eq. (12).

$$^{\cdot}OH + Fe^{2+} \rightarrow OH^{-} + Fe^{3+} \tag{12}$$

It is desirable that the ratio of H_2O_2 to Fe^{2+} should be as small as possible so that the recombination can be avoided and the sludge production from the iron complex is also reduced.

3.2.3. Kinetic studies

The kinetics of degradation reaction of organic pollutants was studied. The degradation of organic pollutants is described by pseudo-first order kinetics reaction as follows:

$$-\frac{dC}{dt} = k_{app}C \tag{13}$$

By integrating this equation at ($t = 0$, $C_t = C_{in}$), Eq. (14) was obtained.

$$-\ln\left(\frac{C_t}{C_o}\right) = k_{app}t \tag{14}$$

where k_{app} is the apparent first order rate constant (min^{-1}), C_o and C_t is the COD concentration of wastewater at a given contact time and t (min), respectively. Kinetic studies were assessed by monitoring the change in the COD level at a certain interval of time (C_t). Apparent first order rate constants (k_{app}) were determined by employing Eq. (14). From the plot of ($-\ln(C_t/C_o)$) versus contact time (t), the k_{app} was determined by calculating the slope of the line obtained. Fig. 5 shows the plott of $-\ln(C_t/C_o)$ against time for homogeneous Fenton oxidation process of flax wastewater at different hydrogen peroxide doses. The reaction kinetics fitted well for pseudo first-order reaction with regression coefficient of 0.98. The apparent rate constants were increased from 0.0037 to 0.0064 min^{-1} as H_2O_2/COD increased from 0.55 to 0.75 (Table 1). On the other hand the corresponding half life time of COD ($t_{1/2}$) decreased to 96 min. The kinetic model suggested that the rate of reaction was controlled by the concentration of hydroxyl radical up to H_2O_2/COD = 0.75.

Fig. 6 showed variation of apparent rate constant (k_{app}) with H_2O_2/COD ratio, there is a significant dependence of k_{app} on hydrogen peroxide ratio. Fig. 7 shows that $-\ln(C_t/C_o)$ plotted against time for homogeneous Fenton oxidation process of flax wastewater at different ferrous ion doses. It was noted that

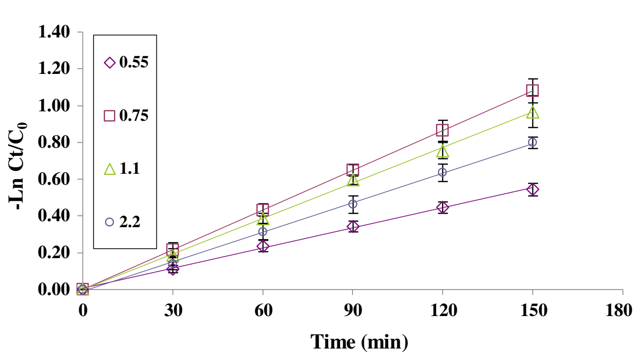

Figure 5 Effects of different hydrogen peroxide doses on Fenton oxidation process of flax wastewater.

Table 1 Kinetic parameters for Fenton oxidation treatment of flax wastewater at H_2O_2/COD ratios.

H_2O_2/Fe^{2+}	k_{app}	r^2	$t_{1/2}$ (min)
0.55	0.0037	0.998	187.3
0.75	0.0072	0.998	96.3
1.1	0.0064	0.997	108.3
2.2	0.0054	0.998	128.4

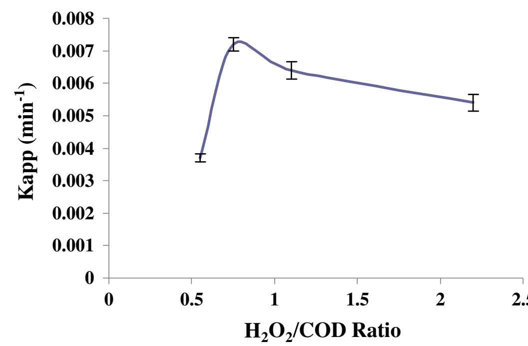

Figure 6 Efects of different hydrogen peroxide doses on apparent rate constant of Fenton oxidation process of flax wastewater.

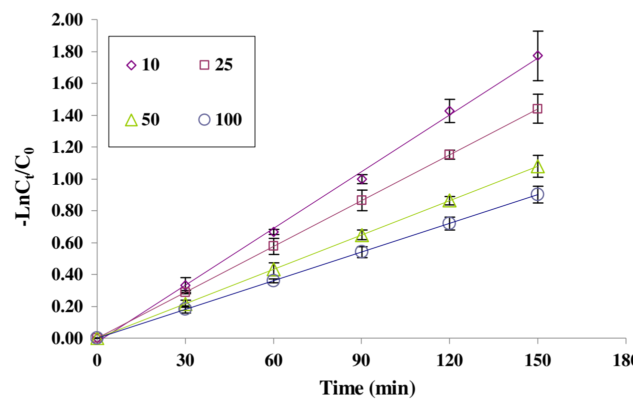

Figure 7 Effects of different ferrous ion doses on Fenton oxidation process of flax wastewater.

k_{app} decreased as the concentration of ferrous ions decreased. Also, as shown in Fig. 8 k_{app} is strongly affected by Fe(II) dose rather than H_2O_2/COD ratio see (Tables 2 and 3).

3.3. Post-treatment using granular activated carbon

The effluent produced after Fenton oxidation treatment still contains considerable amount of organic matters as indicated by residual values of COD (470 mg/L) This value is not fulfilling the National Code of Standard (501/2005) for wastewater reuse or even safe disposal into surface water (HBRC and MHUUC, 2500). Accordingly, post-treatment was employed to remove the residual organic matters from treated wastewater effluent by using granular activated carbon. The adsorption of organic compounds from treated effluent by Activated Carbon (AC) may result from solute hydrophobicity.

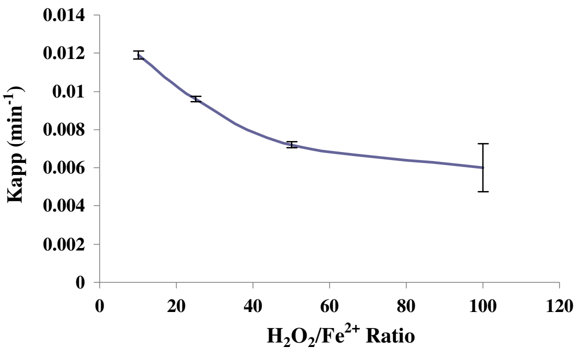

Figure 8 Effects of different ferrous ion doses on apparent rate constant of Fenton oxidation process of flax wastewater.

Table 2 Kinetic parameters for Fenton oxidation treatment of flax wastewater at molar H_2O_2/Fe^{2+} ratios.

H_2O_2/Fe^{2+}	k_{app}	r^2	$t_{1/2}$
10	0.0119	0.998	58.2
25	0.0096	0.999	72.2
50	0.0072	0.999	96.3
100	0.0060	0.998	115.5

3.3.1. Effects of activated carbon doses on treatment of wastewater

The adsorbent dose plays an important role in the adsorption processes for post-treatment of wastewater. Several experiments were carried out with variation in GAC dose from 0.25 to 2 g/L. Fig. 9 illustrated adsorption capacity (q) against GAC doses. The residual COD decreased from 470 to 51 mg/L with increasing dose of adsorbent up to 0.75 g/L, beyond that slight decrease in COD level was achieved. By increasing the dose of adsorbent (GAC) to 2 g/L, the analogue COD removal percent increased from 34.8% to 81%. Thus, the optimal GAC dose was 0.75 g/L from the economic point of view.

3.3.2. Effects of detention time on adsorption efficiency

Adsorption of organics in wastewater by GAC was influenced not only by GAC doses but also by the retention time of adsorbent in the reaction mixture. To determine the optimal retention time of adsorption processes by GAC, experiment was carried out at optimal dose of adsorbent (0.75 g/L) and several

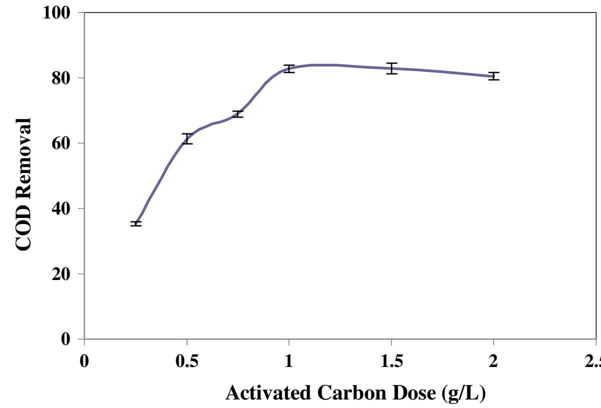

Figure 9 Effects of GAC dose on adsorption treatment of wastewater.

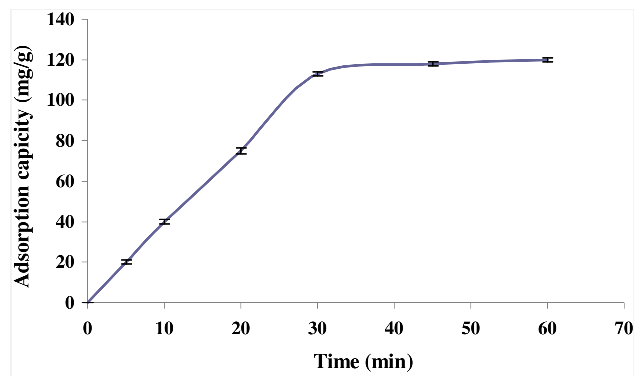

Figure 10 Effects of detention on adsorption treatment of wastewater by GAC.

samples of treated wastewater. Residual COD was analyzed. The obtained data displayed in Fig. 10 show the adsorption capacity (q) against time. Adsorption capacity increased with time as well as COD levels decreased with time. The removal rate of COD was 77% after 30 min and q reached 113 mg_{COD}/g. Thus, the optimal retention time was selected to be 30 min.

3.3.3. Overall efficiency of treatment module

Treatment of retting flax wastewater using Fenton oxidation followed by GAC produced a high quality effluent amenable for reuse in retting process or safe disposal into surface water.

Table 3 Analysis of [a]treated wastewater by Fenton reaction followed by granular carbon.

Parameters	Unit	Raw WW	Treated Effluent	% Removal	[b]Law 48/1982	[c]permissible limits
pH	–	6.1	8.9	–	6–9	6–9.5
COD	mgO_2/L	3133	44	98.6	100	1100
BOD	mgO_2/L	1464	26	98.22	60	600
TSS	mg/L	149	20	86.6	60	800
Ammonia	mgN/L	1.96	N.D	100	–	–
Oil and grease	mg/L	86.5	5	94.22	10	100

[a] Average of five samples.
[b] National limits for wastewater discharge into surface water.
[c] National limits for wastewater discharge into public sewerage system.

The removal efficiencies of COD, BOD TSS and oil & grease were 98.6%, 98.22%, 86.6% and 94.22%, respectively.

4. Conclusion

In this study, combined treatment system of flax wastewater was carried out using Fenton's Oxidation/GAC adsorption. This is first usage of combined AOPs/GAC adsorption for treatment of flax wastewater for reuse. It was noted that Fenton treatment of flax wastewater was highly affected by H_2O_2/COD ratio and Fe^{2+} concentration. The optimum H_2O_2:COD ratio for the oxidation of wastewater was 0.75, while optimum H_2O_2/Fe^{2+} was 50 for less sludge production. Kinetic studies showed that Fenton's treatment of flax wastewater followed a pseudo-first order reaction. Also, it was found that K_{app} was highly affected by H_2O_2/COD and H_2O_2/Fe^{2+} ratios.GAC adsorption was investigated as post-treatment. It was observed that adsorption was highly affected with detention time and GAC dose. Moreover, the proposed treatment module proved to be very effective for the treatment of flax wastewater.

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